O2—Re1—O1	177.0 (3)	177.3 (3)	178.0 (3)
O2—Re1—P1	93.88 (19)	94.3 (2)	93.3 (2)
O1—Re1—P1	89.1 (2)	88.4 (3)	88.7 (2)
O2—Re1—P2	94.75 (19)	94.9 (2)	94.6 (2)
O1—Re1—P2	85.8 (2)	85.5 (2)	85.8 (2)
P1—Re1—P2	86.58 (7)	86.55 (9)	86.37 (9)
O2—Re1—P4	91.66 (19)	91.7 (2)	91.7 (2)
O1—Re1—P4	87.7 (2)	87.8 (2)	87.9 (2)
P1—Re1—P4	95.60 (8)	95.22 (9)	95.43 (9)
P2—Re1—P4	173.08 (7)	173.06 (8)	173.41 (8)
O2—Re1—P3	81.21 (19)	80.8 (2)	81.7 (2)
O1—Re1—P3	95.8 (2)	96.4 (3)	96.3 (2)
P1—Re1—P3	175.05 (7)	175.09 (8)	174.93 (9)
P2—Re1—P3	94.43 (7)	94.36 (9)	94.19 (9)
P4—Re1—P3	83.96 (7)	84.44 (9)	84.58 (9)
P2—Re1—P1—C1	−48.0 (3)	−47.6 (4)	−47.8 (4)
Re1—P1—C1—C2	67.3 (8)	67.4 (9)	66.7 (9)
P1—C1—C2—C3	−77.1 (10)	−77.0 (11)	−76.6 (13)
C1—C2—C3—P2	76.0 (10)	74.7 (11)	75.4 (13)
C2—C3—P2—Rc1	−65.7 (8)	−64.6 (9)	−64.7 (10)
P1—Re1—P2—C3	47.4 (4)	46.9 (4)	46.6 (4)
P4—Re1—P3—C4	34.1 (3)	33.8 (4)	33.2 (4)
Re1—P3—C4—C5	−82.3 (7)	−81.3 (8)	−81.4 (8)
P3—C4—C5—C6	43.3 (11)	41.5 (13)	44.9 (13)
C4—C5—C6—P4	42.1 (12)	42.1 (13)	37.6 (14)
C5—C6—P4—Re1	−74.4 (8)	−73.8 (9)	−71.3 (9)
P3—Re1—P4—C6	23.7 (4)	23.7 (4)	23.6 (5)

The displacement parameters of the perrhenate atoms of compositions $x = 0.17(1)$ and $0.36(1)$ were refined with restraints to avoid unreal values. The water H atoms were neither found nor calculated in any of the three structures.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 1990).

This research was supported by CSIC (Comisión Sectorial de Investigación Científica, Universidad de la República, Uruguay), CONICYT (Consejo Nacional de Investigación Científica y Tecnológica, Uruguay) and PEDECIBA (Programa Especial de Desarrollo de las Ciencias Básicas, Uruguay).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1086). Services for accessing these data are described at the back of the journal.

References

Deutsch, E. A. & Jurisson, S. (1994). *Handbook on Metals in Clinical and Analytical Chemistry*, edited by H. G. Seiler, A. Sigel & H. Sigel, pp. 537-540. New York: Marcel Dekker Inc.

Dilworth, J. R. & Parrott, S. J. (1996). *Current Directives in Radiopharmaceutical Research and Development*, edited by S. J. Mather, pp. 1-29. Dordrecht: Kluwer Academic Publishers.

Hashimoto, K. & Yoshihara, K. (1996). *Top. Curr. Chem.* **176**, 275-291.

Kremer, C., Rivero, M., Kremer, E., Suescun, L., Mombrú, A. W., Mariezcurrena, R., Domínguez, S., Mederos, A., Midollini, S. & Castiñeiras, A. (1999). *Inorg. Chim. Acta*. In the press.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. Version 5.1.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Ram, M. S., Jones, L. M., Ward, H. J., Wong, Y. H., Johnson, C. S., Subramanian, P. & Hupp, J. T. (1991). *Inorg. Chem.* **30**, 2928-2938.

Rouschias, G. (1974). *Chem. Rev.* **74**, 531-566.

Sheldrick, G. M. (1990). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Srivastava, S. C. (1996). *Current Directives in Radiopharmaceutical Research and Development*, edited by S. J. Mather, pp. 63-79. Dordrecht: Kluwer Academic Publishers.

Winkler, J. R. & Gray, H. B. (1983). *J. Am. Chem. Soc.* **105**, 1373-1374.

Yam, V. M., Tam, K. W., Cheng, M. C., Peng, S. M. & Wang, Y. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1717-1723.

Zsolnai, L. & Pritzkow, H. (1995). *ZORTEP. An Interactive ORTEP Program*. University of Heidelberg, Germany.

Acta Cryst. (1999). C**55**, 1789-1791

The salt of the di-μ-chloro-bis[tetrachlorozirconium(IV)] anion with protonated 1,3,5-trimethoxybenzene as cation

SIMON J. COLES,[a] MICHAEL B. HURSTHOUSE,[a] DAVID G. KELLY[b] AND NEIL M. WALKER[b]

[a]*Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England, and* [b]*Department of Chemistry and Materials, Manchester Metropolitan University, Manchester M1 5GD, England. E-mail: s.j.coles@soton.ac.uk*

(*Received 1 June 1999; accepted 28 July 1999*)

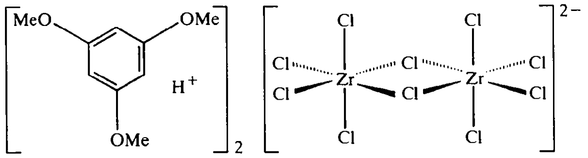
Abstract

The neutrality of the title salt, bis(1,3,5-trimethoxyphenylium) di-μ-chloro-bis[tetrachlorozirconium(IV)], $(C_9H_{13}O_3)_2[Zr_2Cl_{10}]$, is presumably achieved by the addition of a proton to 1,3,5-trimethoxybenzene. This proton was not located crystallographically and is assumed to be disordered over all three methoxy O atoms.

Comment

It is well established that $ZrCl_4$ and other acidic metal species may activate aromatic hydrocarbons to facilitate C—C bond cleavage and intramolecular rearrangement (Solari *et al.*, 1995). The isomerization of methoxy-substituted tetralins *via* $ZrCl_4$-catalysed reactions has also been observed (Harrowven & Dainty, 1996, 1997). In these studies, the formation of η^6-arene intermediates is indicated as being mechanistically significant and is supported by the crystallographic characterization of $[(\eta^6\text{-}C_6Me_6)Zr_2Cl_8]$ (Solari *et al.*, 1995).

In contrast, the reaction of 1,3,5,-trimethoxybenzene with $ZrCl_4$ in dichloromethane results in the isolation of $[C_6H_3(OMe)_3H]_2[Zr_2Cl_{10}]$, (I), in which unique $[C_6H_3(OMe)_3]$ and $[ZrCl_5]$ units were crystallographically characterized. An additional proton (not detected) must be present for each organic molecule to facilitate the formation of this neutral salt. Protonation is likely to result from the reaction of acidic $ZrCl_4$ and adventitious moisture in the nominally dry solvent and inert environment. Since the bond lengths and angles of $[C_6H_3(OMe)_3H]$ here do not differ significantly from those of $[C_6H_3(OMe)_3]$ (Stults, 1979), it is reasonable to suggest that the single proton is located in a disordered manner at all three methoxy O atoms. Chemically, the formation of $[C_6H_3(OMe)_3H]_2[Zr_2Cl_{10}]$ contrasts markedly with the formation of arenes with other aromatic hydrocarbons. Moreover, the very low solubility of the compound in dichloromethane also differs from the significant solubility of the crystallographically characterized $[S_4N_4Cl]_2[Zr_2Cl_{10}]$ (Eicher *et al.*, 1985) and $[Ph_3C]_2[Zr_2Cl_{10}]$ in chlorinated hydrocarbons (Calderazzo *et al.*, 1990). It is this insolubility which may explain the preferential formation of $[C_6H_3(OMe)_3H]_2[Zr_2Cl_{10}]$ in the presence of moisture and the low yield observed.



(I)

The ellipsoid plot (Fig. 1) shows the protonated 1,3,5-trimethoxybenzene and di-μ-chloro-bis[tetrachlorozirconium(IV)] ions. The structure of neutral 1,3,5-trimethoxybenzene has been published previously (Stults, 1979), but a search of the Cambridge Structural Database (CSD; Allen & Kennard, 1983) showed that no structures have been reported where it is protonated as a cation. The CSD also showed previously reported salts of the di-μ-chloro-bis[tetrachlorozirconium(IV)] anion (Eicher *et al.*, 1985; Brusilovets *et al.*, 1995).

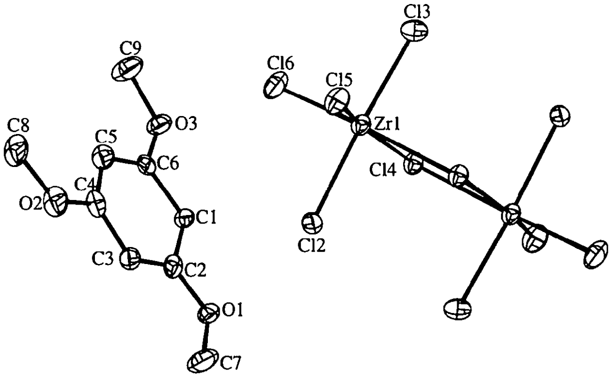


Fig. 1. The structure of the cation and anion of (I) with 50% probability displacement ellipsoids (*CAMERON*; Watkin *et al.*, 1995). H atoms have been omitted.

The bond lengths and angles in (I) deviate little from expected values, with the metal centres in a distorted octahedral coordination geometry and the bridging chloride bonds to zirconium *ca* 0.2 Å longer than the terminal chloride bond lengths. An extensive search with *PLATON* (Spek, 1990) showed there to be no significant intermolecular interactions between the two moieties other than normal coulombic forces.

Experimental

The synthesis of (I) was performed under N_2 using dichloromethane distilled under N_2 from phosphorus pentoxide. 1,3,5-Trimethoxybenzene (1.4 g, 8.3 mmol) in CH_2Cl_2 (5 ml) was added in a single portion to a stirred suspension of $ZrCl_4$ (2.0 g, 8.5 mmol) in CH_2Cl_2 (30 ml). The resultant pale-orange solution was filtered from a fine suspension and cooled to 253 K. Pale-orange crystals of (I) precipitated over a period of *ca* 7 d (0.08 g, 2% yield). Elemental analysis for $C_{18}H_{26}Cl_{10}O_6Zr_2$, expected: C 24.7, H 3.3%; found: C 23.7, H 3.0%; MS $\{FAB\}^+$: m/e = 168 $[C_6H_3(OMe)_3]$.

Crystal data

$(C_9H_{13}O_3)_2[Zr_2Cl_{10}]$
M_r = 875.34
Monoclinic
$P2_1/n$
a = 11.905 (2) Å
b = 9.9448 (14) Å
c = 14.8508 (15) Å
β = 110.079 (10)°
V = 1651.4 (4) Å^3
Z = 2
D_x = 1.756 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 3.29–22.14°
μ = 1.47 mm^{-1}
T = 150 (2) K
Prism
0.28 × 0.22 × 0.11 mm
Orange

Data collection

Nonius FAST TV area-detector diffractometer with an Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986)
ω scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.684, T_{max} = 0.855

5931 measured reflections
2334 independent reflections
1529 reflections with $I > 2\sigma(I)$
R_{int} = 0.095
θ_{max} = 24.29°
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R(F)$ = 0.036
$wR(F^2)$ = 0.147
S = 0.975
2324 reflections
166 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.703 e Å^{-3}
$\Delta\rho_{min}$ = −0.636 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zr1—Cl5	2.3856 (14)	Zr1—Cl2	2.4263 (14)
Zr1—Cl6	2.396 (2)	Zr1—Cl4	2.5949 (13)
Zr1—Cl3	2.4181 (15)	Zr1—Cl4^{i}	2.6184 (14)
Cl5—Zr1—Cl6	101.63 (5)	Cl4—Zr1—Cl4^{i}	77.72 (4)
Cl3—Zr1—Cl2	174.08 (5)		

Symmetry code: (i) $2 - x, -y, -z$.

The data collection strategy nominally covered a hemisphere of reciprocal space by the combination of four scans (φ = 0 and 90° for χ = 0 and 90°) for 0.2° increments in ω, following previously described procedures (Drake *et al.*, 1993). However, higher angle data were very weak and zero or negative intensities were excluded from the refinement, resulting in only 87% completeness.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *MADNES*. Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *CAMERON* (Watkin *et al.*, 1995).

The authors would like to thank the EPSRC for the funding of the National Crystallography Service.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1324). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Brusilovets, A. I., Rusanov, E. B. & Cherniga, A. N. (1995). *Zh. Obshch. Khim.* **65**, 1819–1822.

Calderazzo, F., Pallavicini, P., Pampaloni, G. & Zanazzi, P. F. (1990). *J. Chem. Soc. Dalton Trans.* **9**, 2743–2746.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Drake, S. R., Hursthouse, M. B., Malik, K. M. A. & Miller, S. A. S. (1993). *Inorg. Chem.* **32**, 4653–4658.

Eicher, J., Muller, U. & Dehnicke, K. (1985). *Z. Anorg. Allg. Chem.* **521**, 37–43.

Harrowven, D. C. & Dainty, R. F. (1996). *Tetrahedron Lett.* **37**, 3607–3608.

Harrowven, D. C. & Dainty, R. F. (1997). *Tetrahedron*, **53**, 15771–15786.

Karaulov, A. I. (1992). *ABSMAD. Program for FAST Data Processing.* University of Wales, Cardiff, Wales.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES.* Version II. Enraf–Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Solari, E., Musso, F., Ferguson, R., Floriani, C., Chiesi-Villa, A. & Rizzoli, C. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1510–1512.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stults, B. R. (1979). *Cryst. Struct. Commun.* **8**, 401–403.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Watkin, D. J., Pearce, L. J. & Prout, C. K. (1995). *CAMERON.* Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1999). C**55**, 1791–1793

[μ-*N*,*N*′-Bis(2-pyridylethyl)oxamide]bis[acetatocopper(II)]

REGINA H. P. FRANCISCO,[a] M. TERESA DO P. GAMBARDELLA,[a] ANA M. G. D. RODRIGUES,[a] M. DE PAULA[a] AND GERIMÁRIO F. DE SOUSA[b]

[a]*Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 870, 13560.970 São Carlos SP, Brazil, and* [b]*Departamento de Química, ICC, Universidade de Brasília, 70910.900 Brasília DF, Brazil. E-mail: reginap@iqsc.sc.usp.br*

(*Received 7 January 1999; accepted 9 July 1999*)

Abstract

The structure of the title compound, $[Cu_2(CH_3COO)_2(C_{16}H_{16}N_4O_2)]$, was determined by single-crystal X-ray diffraction and revealed binuclear complex molecules which lie about inversion centers. The Cu^{II} atom has square-pyramidal coordination, with an additional non-bonded Cu···O contact of 2.818 (4) Å, which helps the maintenance of the crystal packing.

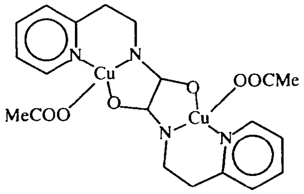
Comment

The chelating properties of *N*,*N*′-disubstituted oxamide ligands revealed four different coordination modes in a number of compounds (Journaux *et al.*, 1985; Zhang *et al.*, 1989, 1996; Lloret *et al.*, 1992; Chen *et al.*, 1994; Sanz *et al.*, 1996; Casellato *et al.*, 1997; Ojima & Nonoyama, 1988).

The diversity of structural possibilities motivated us to study the products of the reaction of *N*,*N*′-bis(2-pyridylethyl)oxamide, H$_2$aepo, with Co^{II}, Cu^{II} and Zn^{II}.

H$_2$aepo crystallizes in a *trans* configuration, and is planar with a center of symmetry in the middle of the ethyl C1—C1^{i} bond [symmetry code: (i) $-x, -y, -z$; Casellato *et al.*, 1997].

During the complexation reaction with Cu(CH$_3$COO)$_2$·4H$_2$O, H$_2$aepo loses its two H atoms. In the product, (I), a binuclear complex, the aepo^{2-} ligand retains the *trans* conformation, with the center of symmetry in the middle of C1—C1^{i} bond, and acts as a bis-tridentate chelate ligand bridging two Cu^{II} ions, which are equivalent by the center of symmetry (Fig. 1).



(I)

Acta Crystallographica Section C
ISSN 0108-2701 © 1999